A Radically New Method for Hydrogen Storage in Hollow Glass Microspheres

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Abstract

Photo-induced hydrogen diffusion has been applied to the problem of storage of high pressure hydrogen in hollow glass microspheres. Results of this study indicate that this phenomenon can be used to provide a high mass efficiency, safe, cheap, non-toxic method for storage of high pressure hydrogen.

The photo-induced response is immediate upon exposure to infrared light for hollow glass microspheres doped with iron, nickel, or cobalt oxide, which is consistent with previous results for transition metal oxide-doped bulk glass samples. This effect is not observed for HGMS which do not contain these transition metal oxide, where the slight release of hydrogen observed occurs only by heating from absorption of the light. The initial rate of hydrogen release increases with increasing concentration of the metal oxide and with increasing hydrogen fill pressure within the microspheres. To date, hydrogen storage efficiencies of 2.2 wt% have been obtained, but results suggest that storage values can be increased to at least 6 wt%. Hydrogen losses over a 5 week period are minimal at room temperature in all compositions, with somewhat greater, but acceptable, losses at 50°C.

Hollow glass microspheres have been produced from an alkali alkaline earth borosilicate glass containing either 1 or 5 wt% of the oxides of iron, nickel, and cobalt. Photo-driven gas diffusion has been demonstrated for these HGMS. Demonstration of photo-induced diffusion in these samples provides the first proof-of-concept for eventual applications of HGMS for large scale hydrogen storage.

Table of Contents

Executive Summary

This project has demonstrated that hydrogen can be stored and delivered using hollow glass microspheres (HGMS) with outstanding efficiency. Improvements in the traditional concept of hydrogen storage in HGMS which result from application of the newly discovered phenomenon of photo-enhanced hydrogen diffusion in glasses have been demonstrated. The ability to store at least 2.2 wt% hydrogen in HGMS is established. The potential for hydrogen densities of at least 6 wt% is reasonable on the basis of this work.

The composition desired for production of hollow glass microspheres (HGMS) for this study was determined by consultation between the subcontractor, MoSci Inc., and the investigators. Following this discussion, MoSci Inc. produced HGMS in approximately 100 gram quantities of a quality sufficient for studies at Alfred University from an alkali alkaline earth borosilicate glass doped with 1 or 5 wt% each of iron, nickel or cobalt oxide. Additional HGMS containing either no dopant or only approximately 0.2 wt% iron oxide as an impurity were produced for comparison to the doped glasses. As produced HGMS have a size distribution ranging from 1 to 140 μm in diameter. Frit of these glasses was also supplied by MoSci Inc. for compositional analysis and for measurement of glass properties.

A mass spectrometer system, or residual gas analyzer (RGA), was constructed, tested, and calibrated for studies of the kinetics of outgassing HGMS. The mass spectrometer was used for comparison of thermally and photo-driven gas diffusion behavior. Thermally and photo-driven diffusion studies using helium and hydrogen have been completed using all HGMS compositions. The reproducibility of the measurement is excellent. The amount of gas which enters the HGMS at equilibrium varies linearly with applied gas pressure during the loading phase of the process. Helium and hydrogen results are in good agreement.

Studies using helium and hydrogen have shown that photo-driven gas diffusion occurs for all of the doped HGMS. Modest heating to approximately 120°C of the sample also occurs during photo-driven outgassing. Photo-induced gas diffusion is observed for both dopant concentrations, but is faster for samples with the larger amount of each oxide. Photo-induced outgassing does not occur in undoped HGMS. Photo-induced ingassing was also demonstrated, suggesting that filling of HGMS to higher pressures can be improved by use of this method instead of the usual method of heating to high temperatures in the presence of high pressure hydrogen.

Studies of the specific wavelength range responsible for the photo-induced hydrogen diffusion effect were carried out by use of optical filters and wavelength dependent reflectors. It has been demonstrated that wavelengths in the range of 1500-2200 nm are responsible for the photo-induced response. It was also found that extended treatments in hydrogen up to 360 hours results in slightly increased photo-driven diffusion in the cobalt and nickel doped HGMS due to changes in the optical absorption spectrum of the glass. No changes occur in the behavior of the iron doped glasses, which do not change color during these treatments. The source of the lamp used to outgas the samples is also important, with much better results obtained for one commercial lamp than for the other.

Hydrogen losses are minimal for samples doped with 5 wt% of FeO, NiO, or CoO and held at either room temperature or 50°C for 5 weeks. Hydrogen losses at room temperature in 5 weeks ranged from 2 to 9 %, with the greatest losses occurring for the Co5 samples. Losses at 50°C in 5 weeks ranged from 7 to 31 %, with the greatest losses again occurring for the Co5 samples. The best hydrogen retention was found for the HGMS doped with FeO, which do not exhibit the best photo-induced outgassing behavior. The best overall results for outgassing behavior and low hydrogen losses are found for the HGMS doped with NiO.

Samples of these HGMS have been successfully filled to 1,500 psi and 5,000 psi with minimal loss from crushing of the microspheres. The strength of HGMS increases with decreasing sphere diameter for these spheres, where the wall thickness is relatively independent of sphere diameter. Results of this study suggest that HGMS with diameters of less than 50 micrometers would be best for hydrogen fill pressures approaching 10,000 psi. There is no evidence in this work that fill pressures cannot be increased to the desired range of 10,000 psi.

Introduction

This project has demonstrated that hydrogen can be stored and delivered using doped hollow glass microspheres (HGMS) with outstanding efficiency. Improvements in the traditional concept of hydrogen storage in HGMS which result from application of the newly discovered phenomenon of photo-enhanced hydrogen diffusion in glasses have been demonstrated. The ability to store at least 2.2 wt% hydrogen in HGMS is established.

This report will present the details of the study carried out at Alfred University during the past 3 years. It is shown that the use of a dopant is essential in obtaining the photo-induced hydrogen diffusion effect and that this method is superior to the older thermal method proposed in the past. Production of HGMS is well established and can be extended to commercial quantities on demand.

A large number of experimental variables were examined in this study, including the identity and concentration of dopants, lamp intensity, source of the lamp, determination of the most efficient wavelength of light for this process, gas retention in the HGMS at room temperature and 50°C, size of the HGMS used in the diffusion experiment, and the effect of high pressure gas on the process.

Experimental Procedures

Characterization of Hollow Glass Microspheres

HGMS were produced by the MoSci Corporation specifically for this project. Commercial amber glass frit was used to produce the amber, Fe1, Fe5, Ni1, Ni5, Co1 and Co5 microspheres, so a small amount of Fe_2O_3 (~0.2 wt%) is inherent to each of these compositions in addition to any dopant added. The undoped HGMS were formed using colorless commercial container glass frit instead of amber glass frit. HGMS were prepared by a proprietary flame spheroidization method.

Density of the HGMS was measured by placing microspheres of each composition in a plastic vial of known volume (1.5×10^{-5} m^3). Sample vials were lightly tapped on a tabletop to ensure better particle packing. The mass was recorded and bulk densities were calculated. True HGMS densities were determined using a calibrated Micromeritics AccuPyc 1330 helium pycnometer. The average of three measurements was taken for each sample.

Samples were examined by scanning electron microscopy. A sample stub covered

with a piece of carbon tape was placed face down on a piece of wax paper containing a thin layer of HGMS. Care was taken to avoid putting pressure on the stub to ensure that microspheres were not broken. Excess HGMS were removed from the stub by gently tapping the edge on a hard surface. The samples were coated with a Au – Pd alloy. Images of microspheres for diameter measurements were primarily taken using a FEI Quanta 200F Environmental Scanning Electron Microscope (ESEM) in back scattered electron (BSE) and secondary electron (SE) mode using a 4 nm spot size and 25 kV acceleration voltage. Additional images were also made using a Philips scanning electron microscope (SEM) in SE mode using a 100 nm spot size and 20 kV acceleration voltage. HGMS were crushed using a mortar and pestle for the wall thickness measurements; images were made using the parameters listed for the Philips SEM.

The diameters of approximately 200 microspheres of each composition were measured using ImageJ 1.36b software. Wall thickness measurements were much more difficult, as not all fragments were representative of the true wall thickness due to their orientation or fracture surface. Between 15 and 20 fragments were measured for each composition using the ImageJ 1.36b software.

HGMS were examined for possible crystallinity by crushing with a mortar and pestle until a powder was obtained. The powder was placed on a zero background holder containing a thin layer of Vaseline. Excess powder was removed by gently tapping the sample holder on a hard surface. X – ray diffraction patterns were collected using $CuK\alpha_1$ radiation in a Philips PW 1800 X – ray Diffractometer from 10 – 70°2θ, with a 0.02° step size and a 3 second dwell time.

Gas Kinetics and Content Measurements

A Stanford Research Systems RGA100 Residual Gas Analyzer, connected to the vacuum system shown in Figure 1, was used to monitor changes in gas partial pressure via mass spectrometry. The system has been slightly modified by the author in order to accommodate the smaller sample tubes used for HGMS outgassing experiments.

A borosilicate sample tube containing filled HGMS was attached to the system, in which all valves were initially closed, except for valve “B”. The diffusion pump was switched to the “closed” position, while the vacuum pump was placed in “roughing” mode to remove air from the system. Valve “E” was opened to evacuate the sample tube and, when the thermocouple gauge read approximately 30 mTorr, the vacuum pump was switched to the “backing” position and the

diffusion pump was opened. When the digital pressure gauge dropped to ~ 1 – 2 × 10^{-5} Torr, valve "A" was opened and as the pressure approached 4 – 5 × 10^{-6} Torr, the filament was turned on using the SRS RGA 2.2 software. An experiment was started at a pressure of approximately 1 × 10^{-6} Torr. Three hundred seconds of background were collected before a preheated furnace was raised around the sample tube or prior to lamp exposure. In photo – outgassing experiments a 250 W heat lamp was positioned so that the HGMS were approximately 254 mm (1 inch) away from the center of the bulb. Either a colorless GE 250 W heat lamp (Product Code: 37770) or a colorless Sylvania 250 W infrared lamp (Product Number: 14665) was used with one of the fixtures shown in Figure 2. It should also be noted that a semicircular aluminum foil reflector was placed behind the sample tube in order to maximize the amount of light reaching the microspheres. Figure 3 demonstrates the need for a reflector during photo – outgassing experiments. At the end of an outgassing experiment (typically 30 minutes), the filament was turned off and valves "A" and "E" were closed, while valve "F" was opened to vent the sample tube to air. The furnace was lowered or the lamp was shut off and the sample tube was allowed to cool to room temperature.

In order to quantify the amount of gas being released from a sample, a calibrated leak standard[1] must be used. The standard vessel was attached to the system as shown in Figure 1 and the system was prepared for an experiment as described in the previous section. Valve "D" on the leak standard was opened in addition to valve "E" to relieve any pressure buildup in the cylinder. Just before the collection of background, valve "D" was closed and then reopened after 300 seconds. After 30 minutes of data collection, valve "D" was closed and the system was ready for a typical thermal or photo – outgassing experiment. An outgassing curve from a hydrogen leak standard (6.87 × 10^{-6} mL/s) is shown in Figure 4 and a sample thermal outgassing curve is shown in Figure 5. The backgound leveled measured for the first 300 seconds is subtracted from the entire curve and area is calculated between 300 and 2100 seconds (Δt), unless otherwise noted. The amount of gas released (X) during a specified amount of time is given by

$$X = \frac{\text{(Leak Standard Flow Rate)*(Sample Area)*}(\Delta t)}{\text{Leak Standard Area}} \qquad (1)$$

Results are typically expressed as molecules of hydrogen and are adjusted by sample mass and fill pressure.

[1] Vacuum Instrument Corporation. Ronkonkoma, NY.

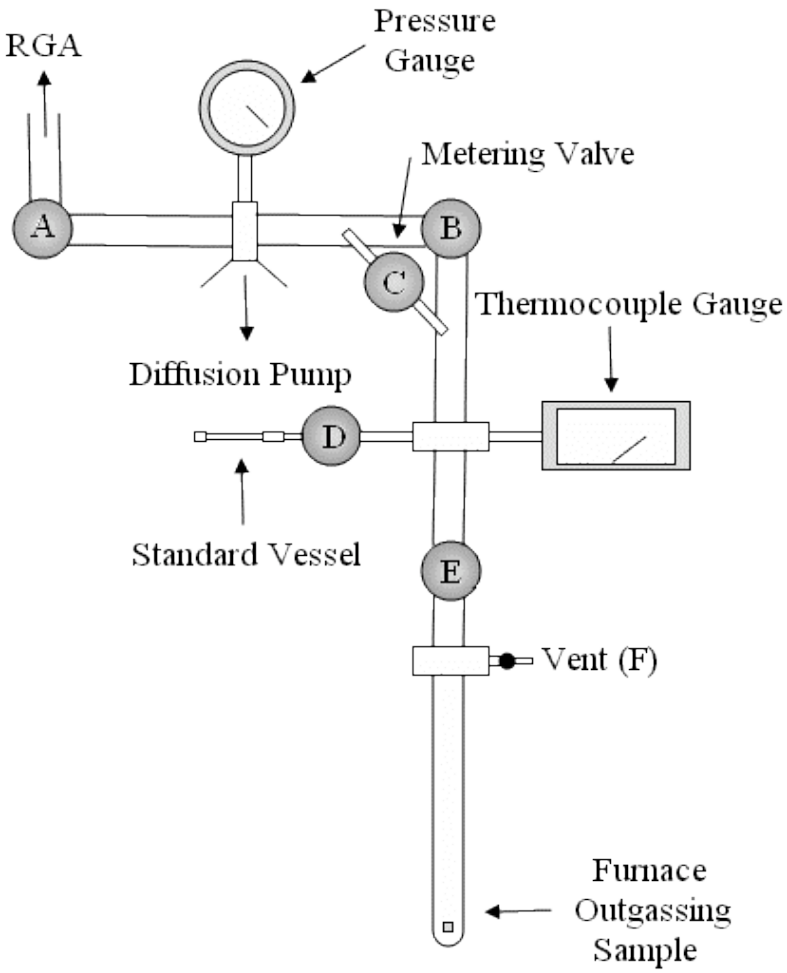


Figure 1. Schematic of the mass spectrometer.

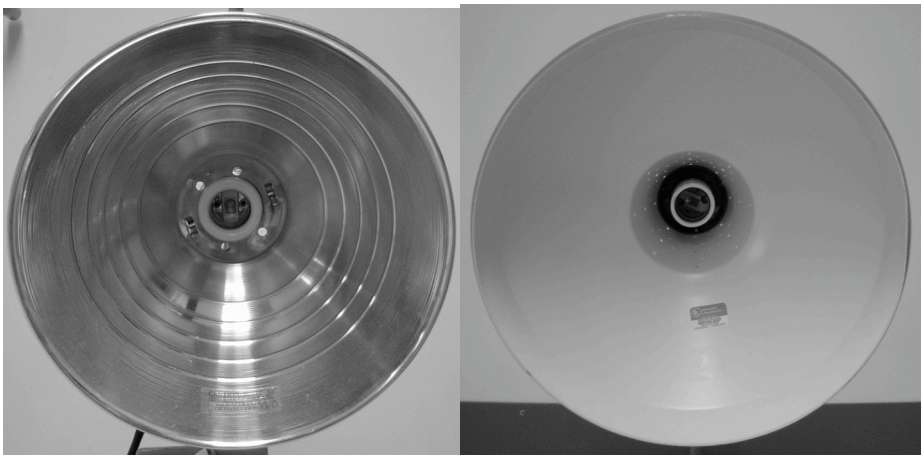


Figure 2. Images of lamp fixtures used during photo – outgassing.

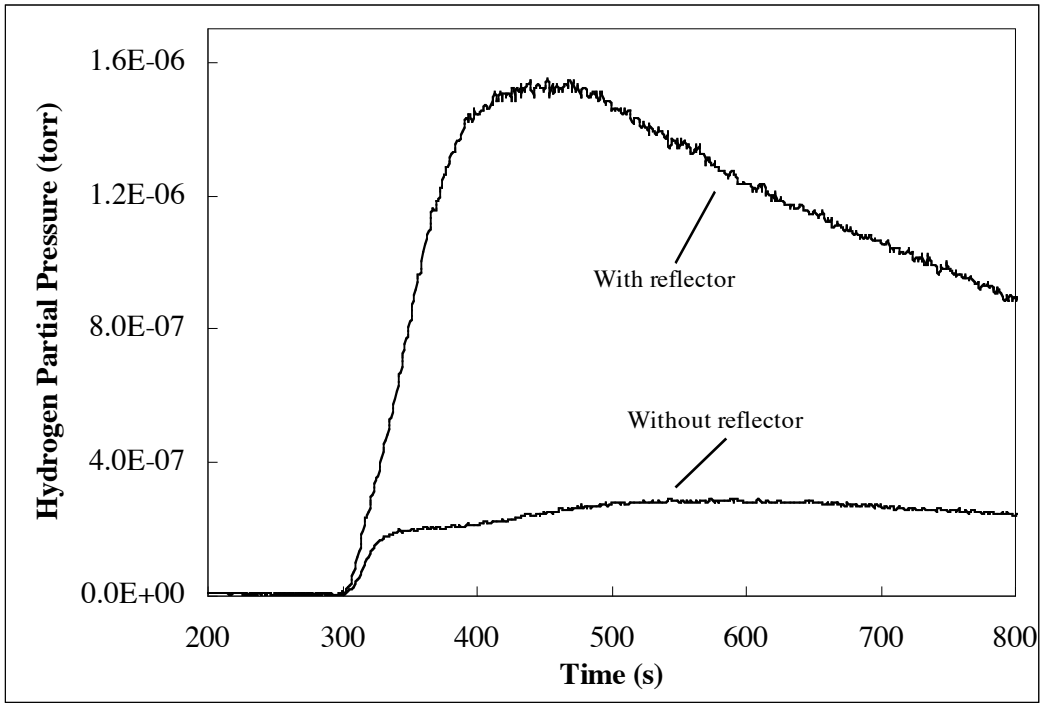


Figure 3. Effect of use of a reflector on photo – outgassing from Co5 HGMS.

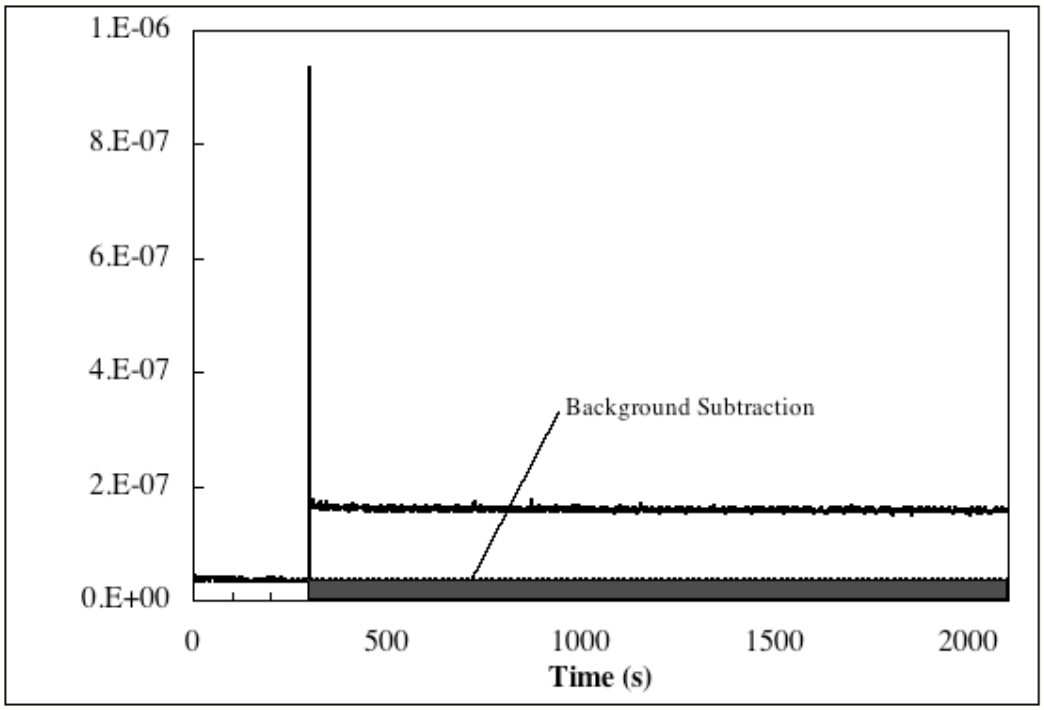


Figure 4. Outgassing curve from a hydrogen leak standard with a flow rate of 6.87 $\times 10^{-6}$ mL/s.

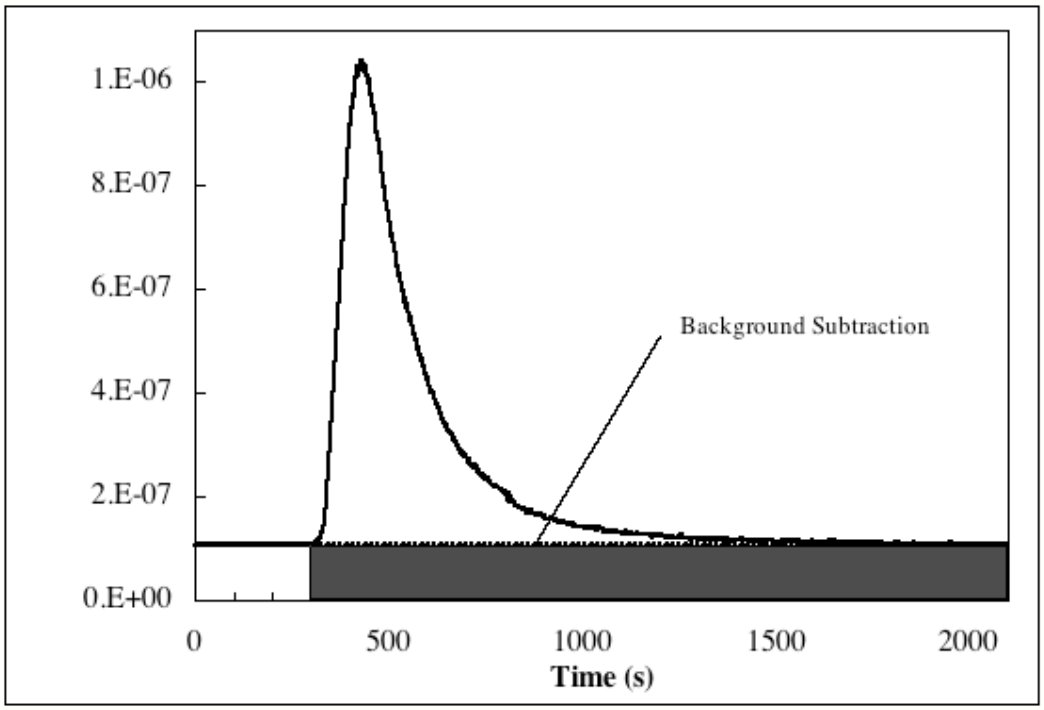


Figure 5. Hydrogen outgassing curve from undoped microspheres.

Results and Discussion:

This project began on September 1, 2004. During this project, MoSci Inc. produced HGMS of all compositions/dopant levels, apparatus for these studies was constructed, tested, and calibrated, and photo-enhanced diffusion studies were completed. It has been clearly demonstrated that NIR light in the range of 1500-2200 nm is responsible for the photo-induced hydrogen diffusion effect.

Kinetic measurements of outgassing of HGMS under both thermally and photo-driven conditions were measured using mass spectroscopy via a residual gas analyzer (RGA) in which the partial pressure of the gas is measured continuously with time. This apparatus allows for outgassing measurements using small quantities (≤ 0.2 g) of HGMS containing 700 torr of hydrogen. Quantities as low as 0.01 g are needed for HGMS containing 5,000 psi of hydrogen. This method cannot be used when the partial pressure of the gas exceeds the system upper limit of 1×10^{-3} torr.

A micrograph of a representative sample of HGMS taken using a scanning electron microscope is shown in Figure 6. The as-received samples contain very few broken shells. These micrographs represent samples which were deliberately crushed to

produce a small fraction of broken shells so that the wall thickness could be measured.

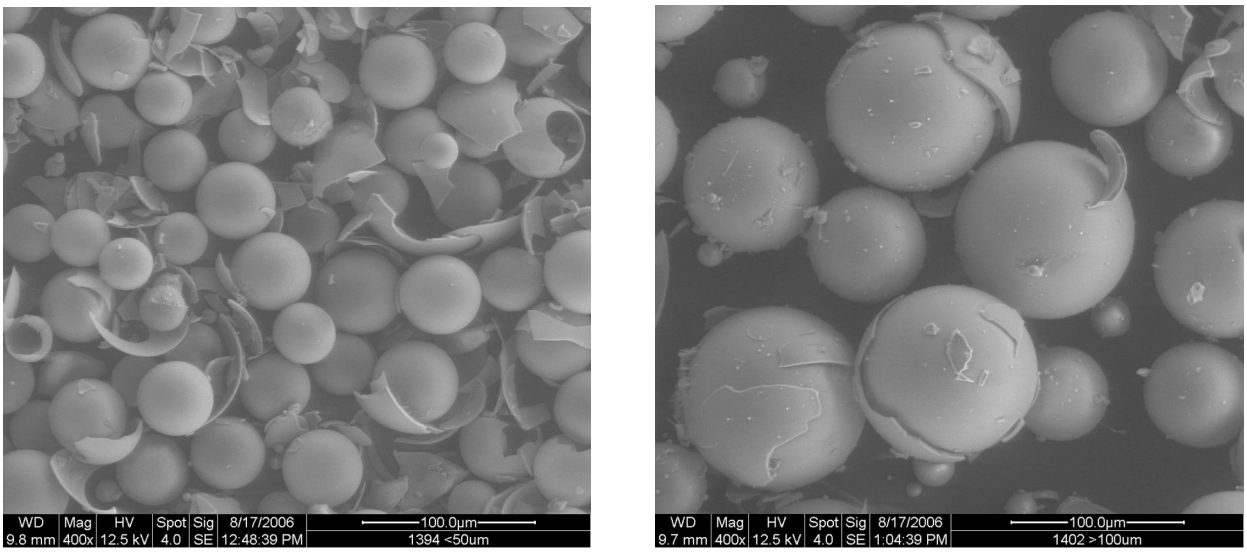


Figure 6. Electron micrographs of HGMS used in this study.
HGMS were crushed in order to determine wall thickness.

A series of initial studies using helium were carried out using 5 wt% iron – doped HGMS. A series of measurements of the reproducibility of the outgassing curves obtained for identical conditions (300°C and 700 torr fill pressure) are shown in Figure 7.

The relation between the amount of gas which enters the HGMS at equilibrium and the applied gas pressure was determined using hydrogen Figure 8. As expected, the amount of gas contained within the HGMS varies linearly with applied gas pressure during the loading phase of the process.

A comparison of thermal outgassing at 400°C and photo outgassing is shown in Figure 9 for 5 wt% nickel oxide-doped HGMS. The HGMS were filled with hydrogen by exposure to 700 torr of hydrogen at 400°C. A lag time is associated with thermal outgassing, however, photo – induced outgassing results in the immediate release of hydrogen. Identical behavior is observed for iron and cobalt oxide-doped HGMS. Although the amount of hydrogen released during thermal and photo – induced outgassing is comparable, the gas partial pressure during photo - outgassing returns to background much more quickly than thermal outgassing.

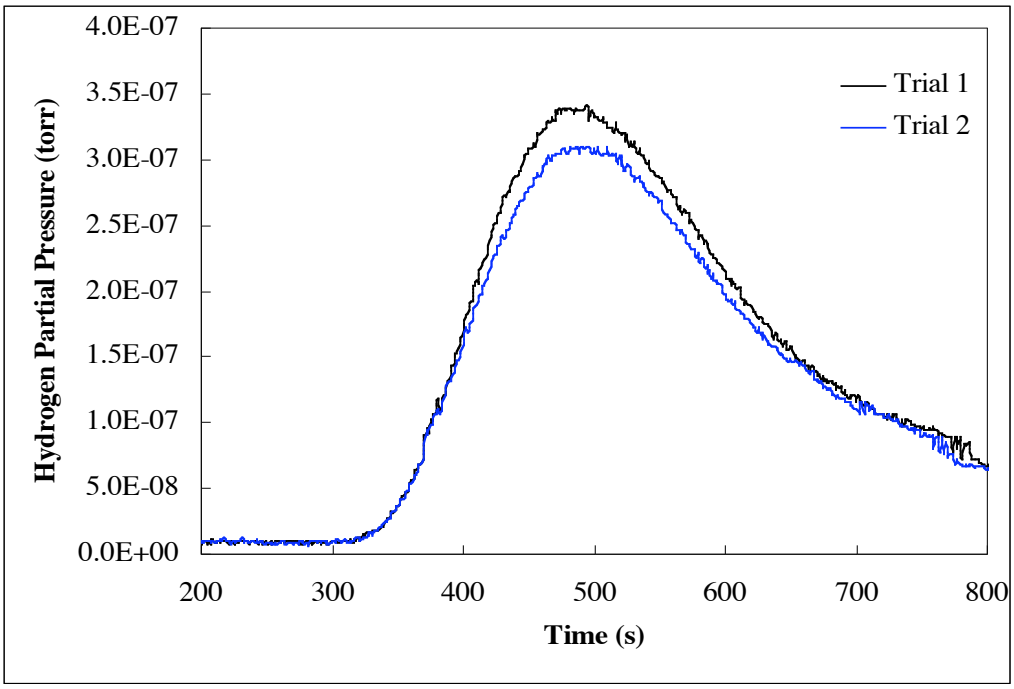


Figure 7. Helium outgassing curves for the same sample of 5 wt% iron oxide-doped hollow glass microspheres at 300°C.

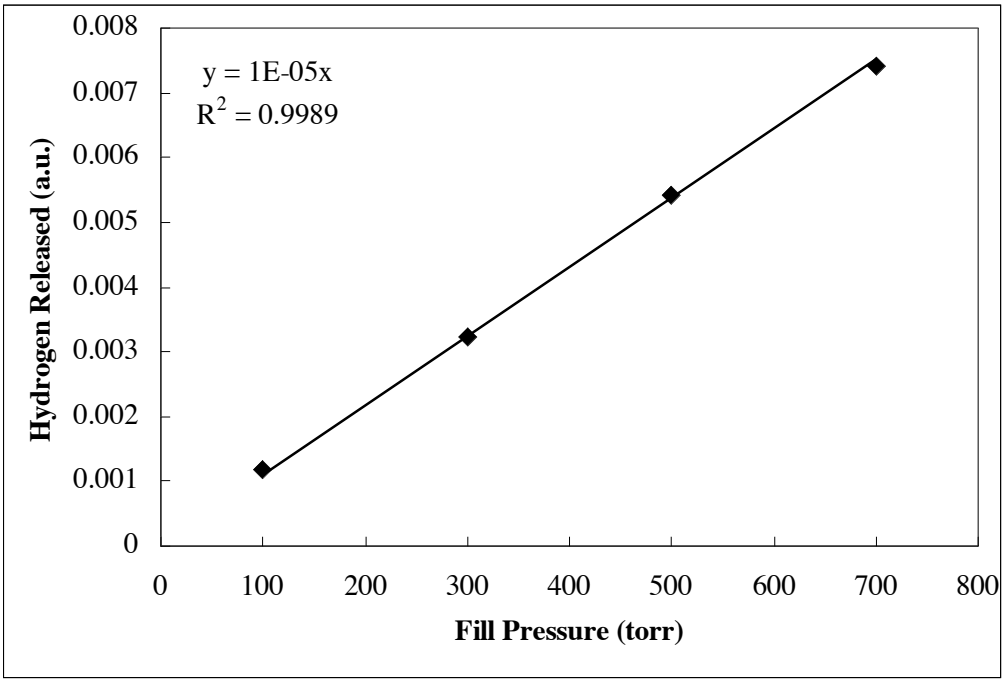


Figure 8. Total gas released from a set of undoped HGMS filled to various pressures at 400°C and outgassed at the same temperature.

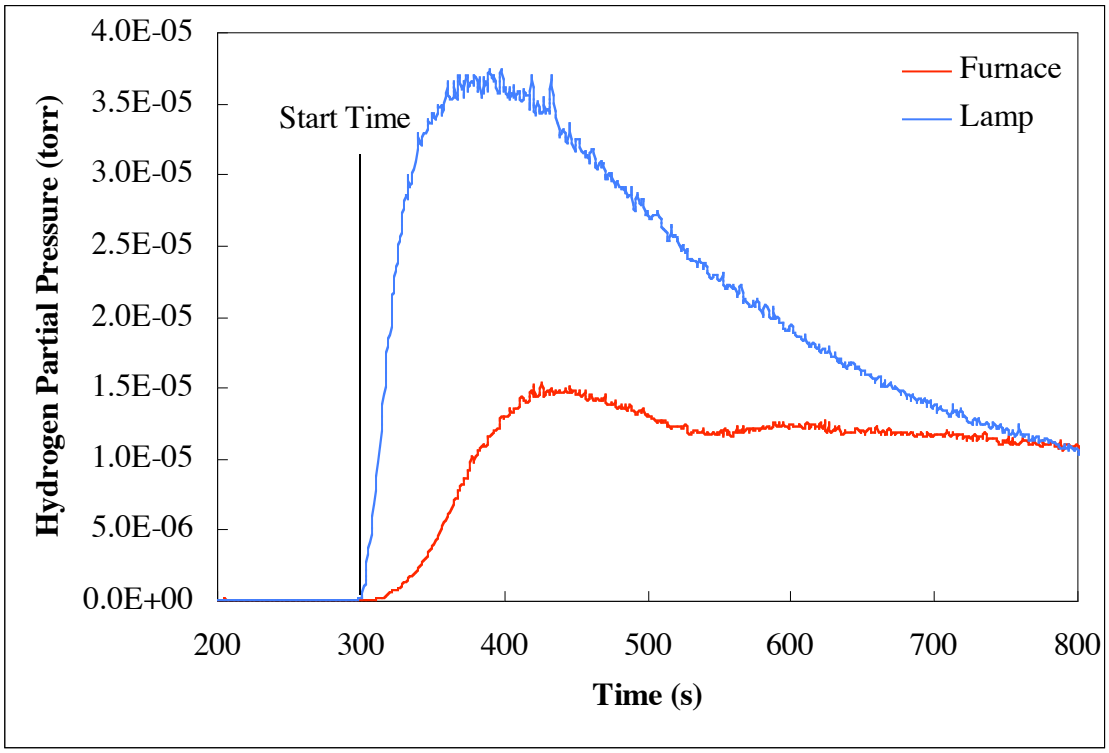


Figure 9. Comparison of thermal (400°C) and photo-induced outgassing for 5 wt% nickel oxide-doped HGMS filled in 700 torr of hydrogen at 400°C.

Limited heating of the sample during photo-induced outgassing does occur over extended time of exposure to the light. Measurement of the temperature of the HGMS at equilibrium, using an infrared thermometer, indicates that the HGMS reach a temperature of approximately 120°C and never exceed a temperature of 150°C. The time to reach this temperature is at least 5 minutes. While this measurement method is subject to error, it is certain that the HGMS do not reach temperatures near 400°C (temperature of thermal outgassing) during photo-outgassing. Since the HGMS are at room temperature when the lamp is turned on, the immediate hydrogen release cannot be a result of a thermal effect. The mechanism for photo-induced outgassing is still unknown, but may be related to the excitation of a transition metal – hydrogen bond caused by infrared radiation. Coupling of the phonon spectrum of the glass to the light frequency would allow expansion of local bonds, opening the doorways between interstices, and allowing dramatically increased gas mobility. Studies of the effect of doorway diameter on gas diffusion in glasses suggest that an increase in doorway diameter of only a few hundredths of a nm are needed to increase the hydrogen diffusivity by several orders of magnitude.

The influence of dopant identity and concentration on photo-induced hydrogen outgassing was determined for all compositions. A comparison of photo-outgassing from all compositions is shown in Figure 10. Outgassing is immediate for both the 1 and 5 wt% doped samples, with little or no difference in the onset time of outgassing as shown in Figure 11. As expected, very little hydrogen is released from the undoped HGMS. The small amount of hydrogen release can be attributed to heating from the lamp due to the small amount of iron oxide in the undoped glass. Measurements of the iron-free HGMS show even less photo – induced outgassing.

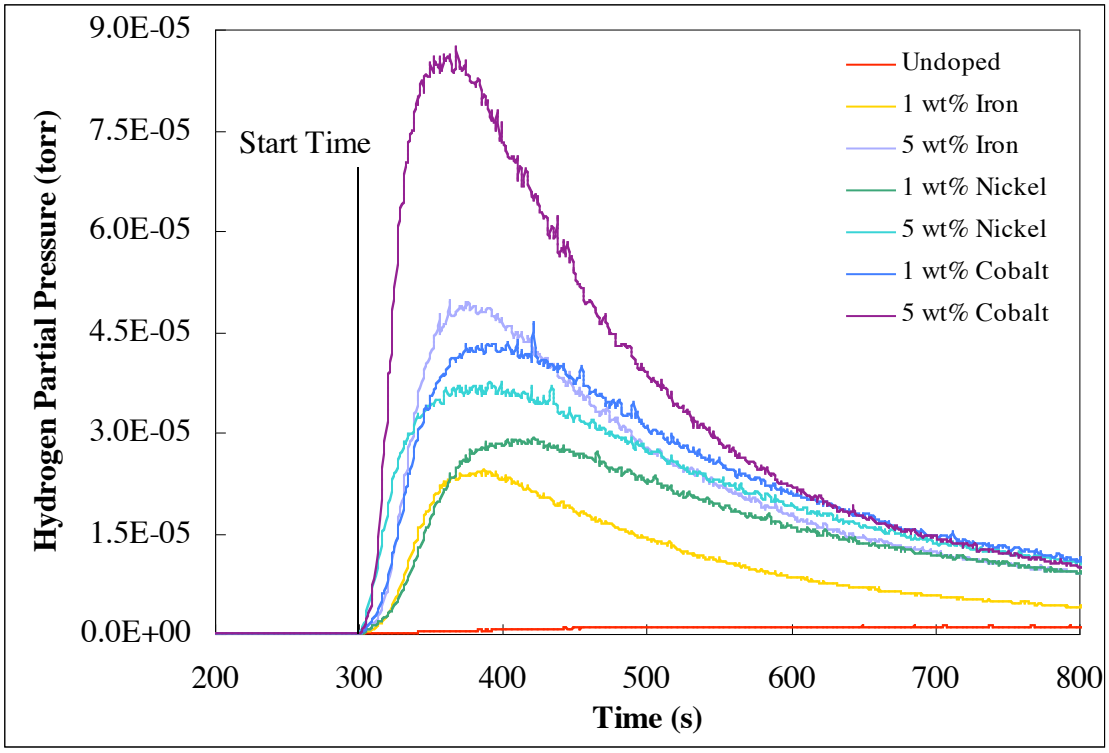


Figure 10. Comparison of hydrogen photo-outgassing from undoped HGMS and 1 and 5 wt% doped HGMS.

HGMS are known to become more resistant to crushing under high gas pressures as the diameter decreases. Studies of the effect of HGMS diameter were carried out by sieving the HGMS to separate them into samples with the following size ranges: < 50 µm, 50 - 75 µm, 75 – 100 µm and > 100 µm. There tends to be a small increase in the amount of hydrogen released during photo-outgassing with increases in microsphere diameter, although a few small deviations from this trend

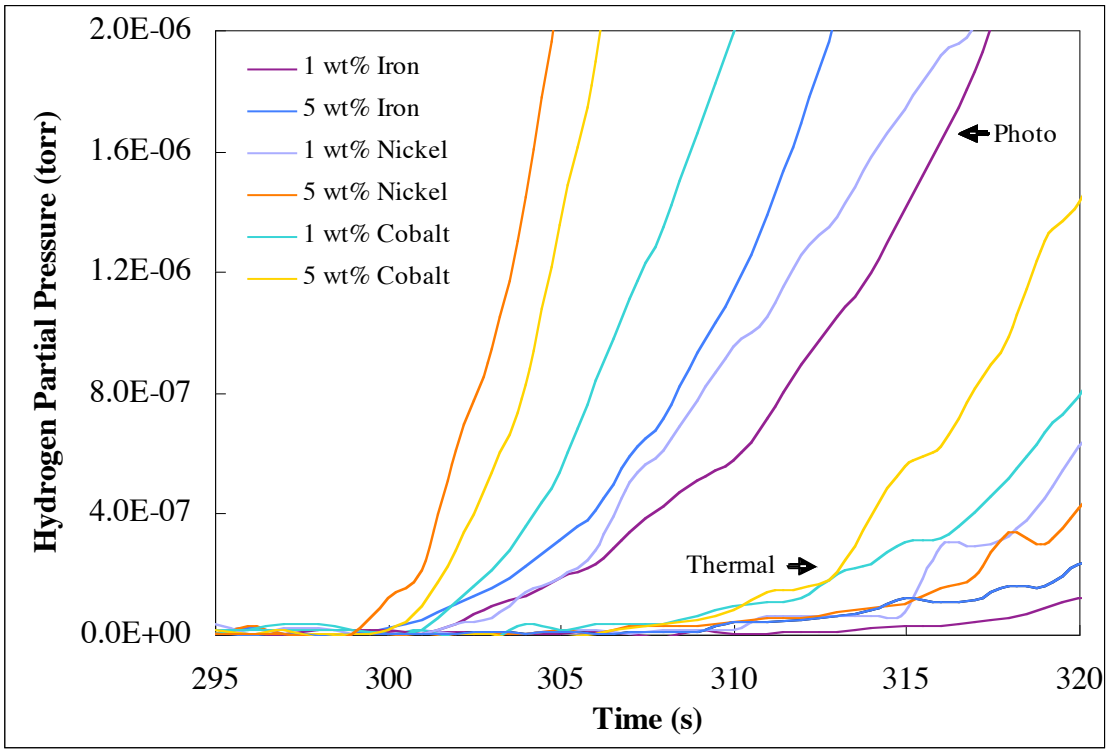


Figure 11. Initial photo-outgassing behavior from all doped HGMS. Thermal outgassing has been included for comparison.

were observed. This behavior is expected as the internal volume of a HGMS increases with an increase in diameter. A comparison of the amber, 5 wt% iron and cobalt-doped HGMS are shown in Figure 12. No data are available for the completely undoped and 5 wt% nickel oxide-doped HGMS due to the high fraction of microspheres having diameters greater than 100 μm, i.e. there was an insufficient quantity of smaller HGMS available to form acceptable samples. While the amount of gas contained within the microspheres is a function of sphere diameter, the diameter does not appear to have an influence on the initial rate of photo-outgassing of any of the compositions.

Samples doped with 5 wt% iron, cobalt and nickel were tested for response to the light by exposure to the lamp radiation for either 5 minute and 30 second intervals, followed by covering the light for the same time intervals. The expose/cover sequence was repeated several times. All compositions exhibit rapid switching behavior in which gas release is immediate upon lamp exposure and ceases when the lamp is covered as shown in Figures 13 and 14 for the 5 wt% iron-doped HGMS. The trends are identical for 5 wt% cobalt and nickel-doped HGMS. Switching behavior further strengthens the argument that the photo-induced

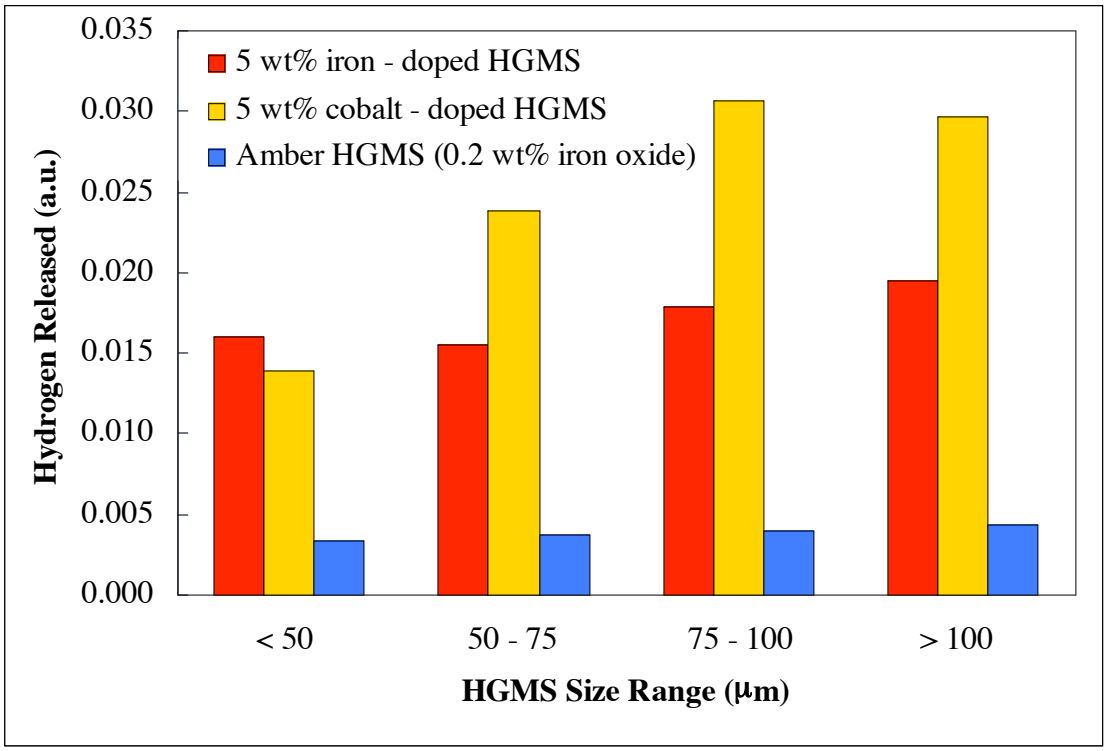


Figure 12. Comparison of the hydrogen released during photo - outgassing as a function of HGMS size.

response is not solely due to a thermal effect. During 5 minutes of exposure to the light, there is some heating of the sample, but during a 30 second exposure, it is probable that samples reach no more than 75°C. Such a low temperature cannot account for this outgassing response behavior.

Photo-outgassing was studied as a function of lamp intensity by varying the voltage from 20-120 V. The amount of hydrogen released increases exponentially with applied voltage, i.e. light intensity, as shown Figure 15 for 5 wt% nickel oxide-doped HGMS. A similar trend is observed for 5 wt% iron and cobalt oxide-doped HGMS.

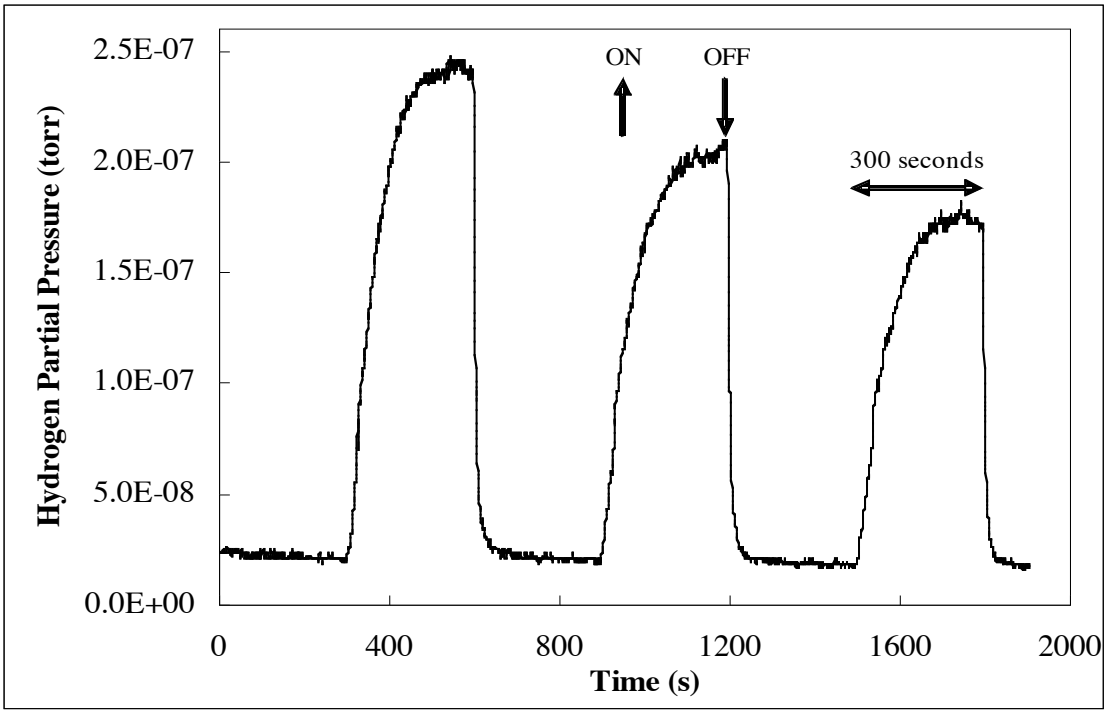


Figure 13. Photo-outgassing in 300 second intervals from 5 wt% iron-doped HGMS filled with 700 Torr of hydrogen at 400°C.

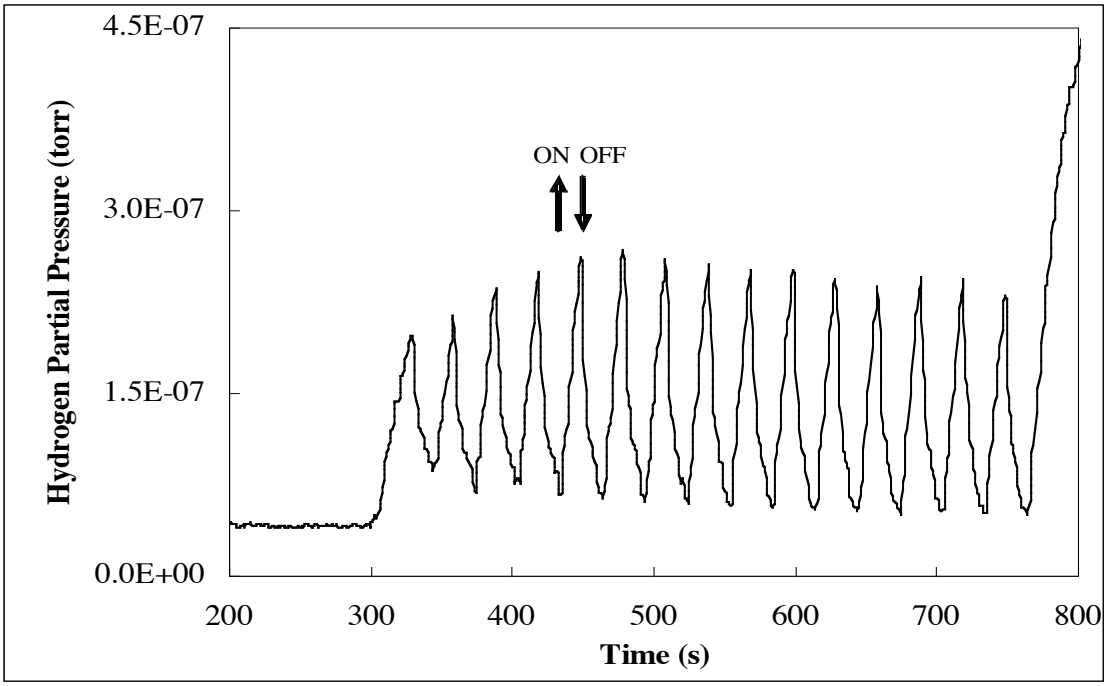


Figure 14. Photo-outgassing in 30 second intervals from 5 wt% iron-doped HGMS filled with 700 Torr of hydrogen at 400°C.

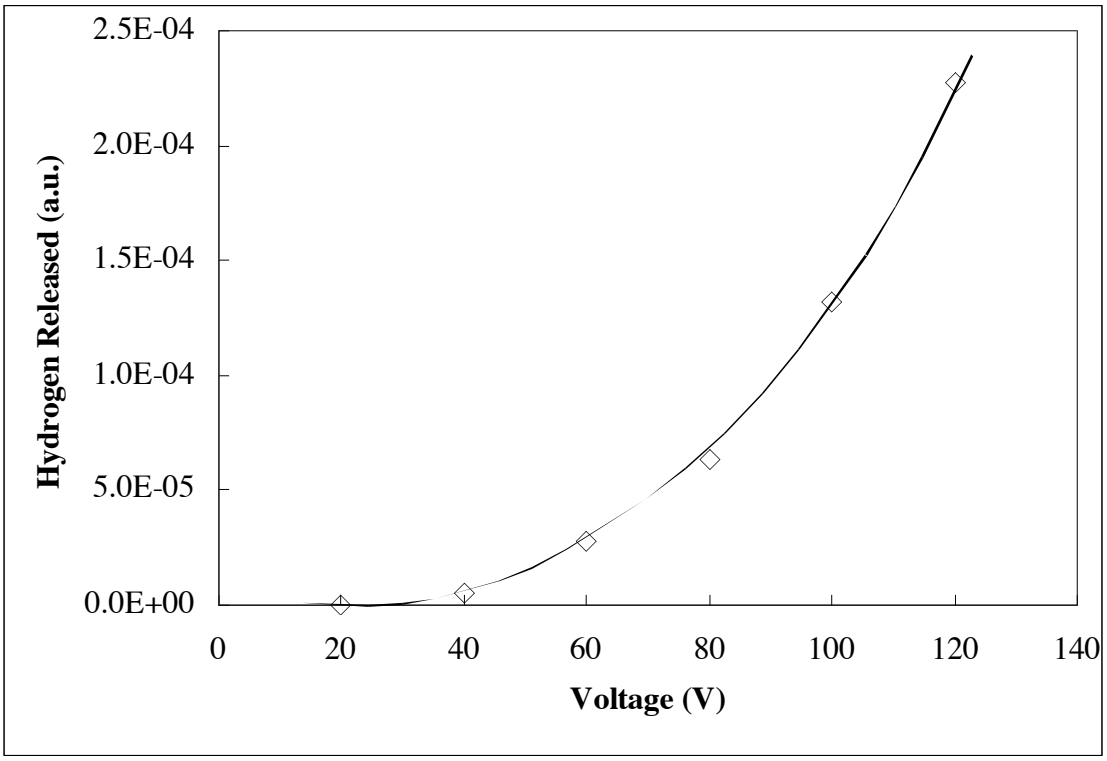


Figure 15. Outgassing curves as a function of voltage for 5 wt% nickel-doped HGMS.

Two different 250 W infrared bulbs were tested during this work; a colorless Sylvania 250 W incandescent infrared lamp and a colorless GE 250 W Heat Lamp. Aside from differences in filament design, the bulbs appear identical. In addition, two different fixtures were used, yielding the results shown in Figure 16. A comparison of the various bulb/fixture combinations and thermal outgassing is shown in this figure for 5 wt% nickel oxide-doped HGMS. The Sylvania bulb significantly improves photo-induced outgassing, while there is little difference between fixtures. Comparable behavior is observed in 5 wt% iron and cobalt oxide-doped HGMS. Limited Visible-NIR spectra of the bulbs were measured and are shown in Figure 17. A method for measurement above 1000 nm is not available at this time, so the spectra of the bulbs in the important NIR region is not available. The outputs of the bulbs in the range of 400 – 900 nm are almost identical, but at wavelengths of 925-1000 nm, the output of the Sylvania bulb is larger. This behavior agrees with other tests (discussed below) that the visible region has little or no influence on the photo-induced response.

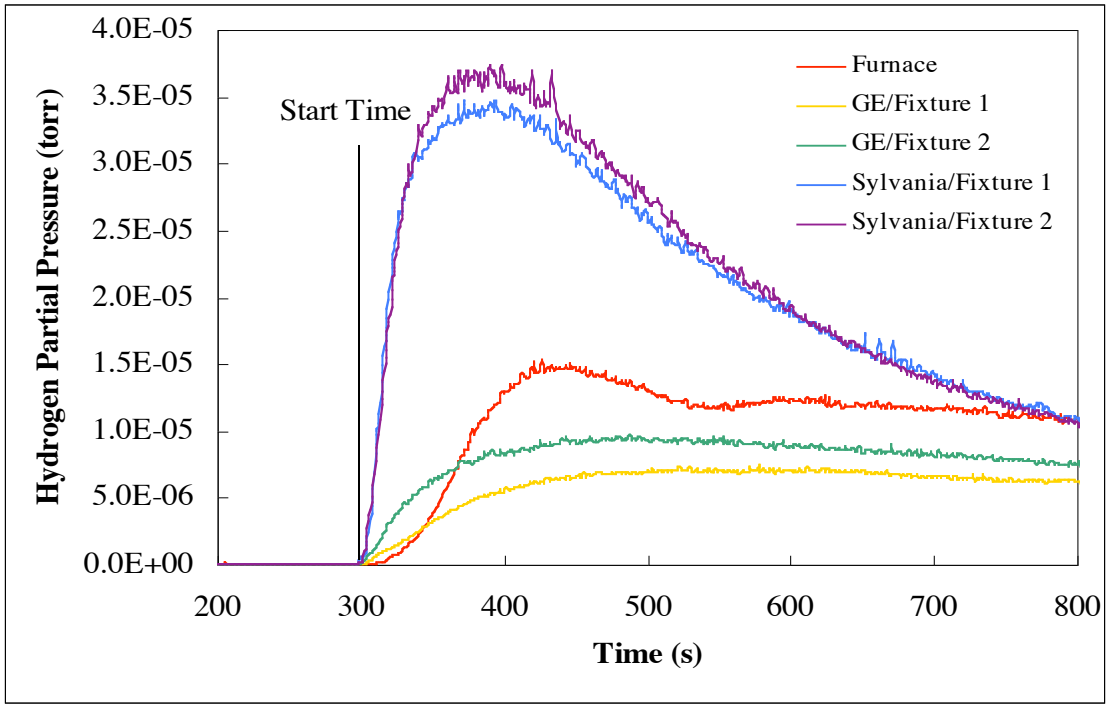


Figure 16. Comparison of the various bulb/fixture combinations for photo-induced outgassing and thermal outgassing (400°C) for 5 wt% nickel oxide-doped HGMS.

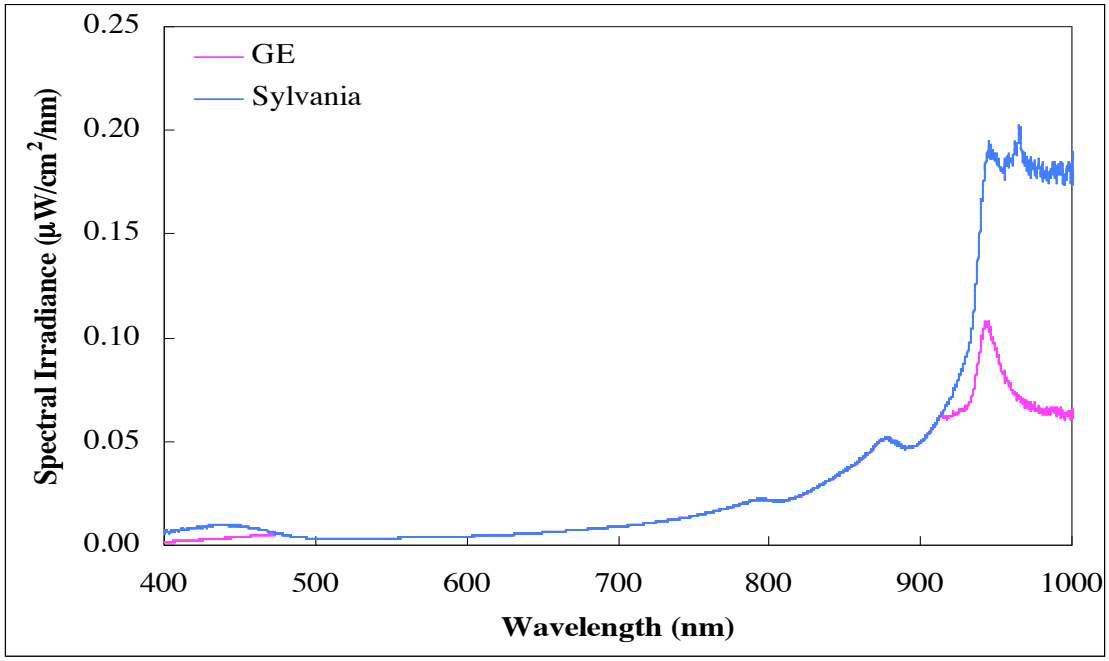


Figure 17. Visible-NIR spectra of the GE and Sylvania 250 W bulbs.

Absorption filters and reflective mirrors were used to control the wavelengths of light reaching the 5 wt% iron, nickel and cobalt oxide-doped HGMS. The visible-NIR spectra of these materials are shown in Figures 18 and 19. A filter/mirror holder (Figure 20) was attached to a ring stand to position the filter or reflective mirror between the sample and the lamp. The influence of reflective mirrors and absorption filters on the photo-outgassing behavior of hydrogen-filled 5 wt% nickel-oxide doped HGMS is shown in Figure 21. "None" refers to the photo-outgassing curves collected for the empty filter/mirror holder. There is a considerable reduction in the hydrogen released when the hot extended mirror and filter 5030 are used, whereas only a small decrease is observed with the cold and hot mirrors, as well as filter 2563, as compared to the "None" curve. Comparable behavior is observed for the 5 wt% iron and cobalt oxide-doped HGMS. The filters and mirrors exhibit very different characteristics in the range of 200-1200 nm. It appears that these wavelengths have little or no effect on the photo-induced response, which corresponds with the spectral data from both bulbs. Use of filter 5030 reveals the most information, as its transmission is drastically reduced between 1500 and 2200 nm, resulting in very little hydrogen release during photo-outgassing in all 5 wt% doped samples. These results indicate that wavelengths in the range of 1500-2200 nm are most responsible for the photo-induced response.

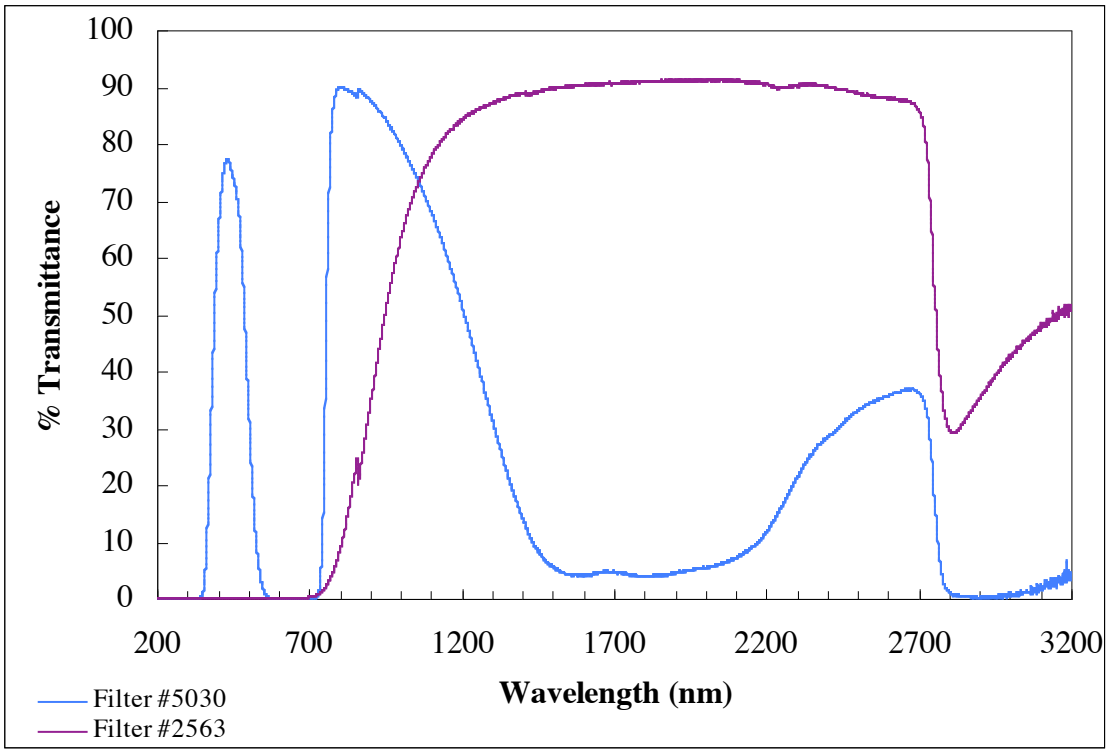


Figure 18. UV-Vis-NIR transmission spectra of absorption filters 2563 and 5030.

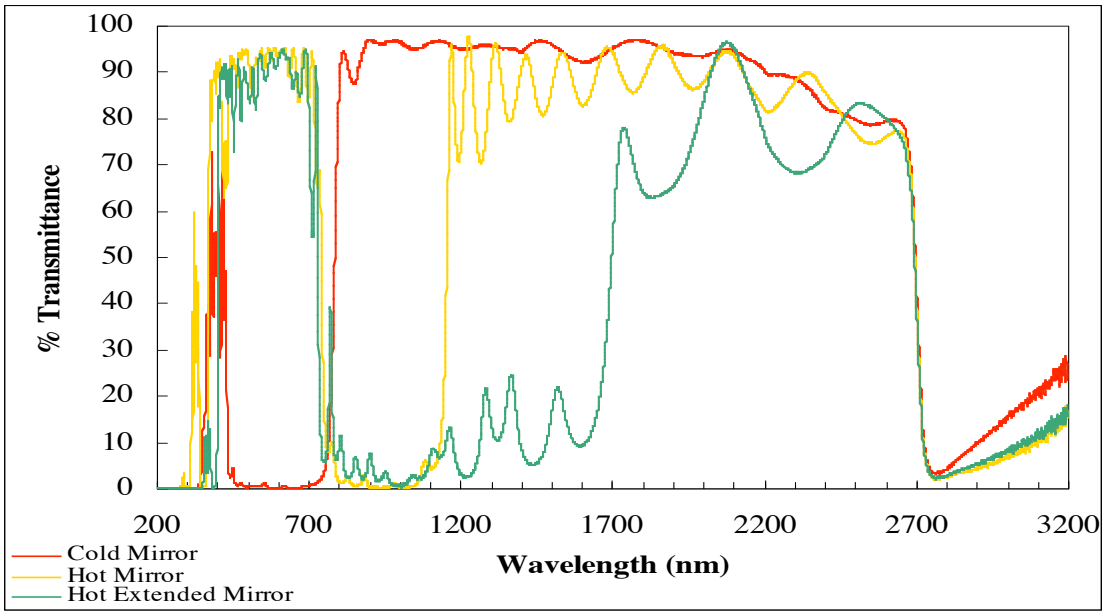


Figure 19. UV-Vis-NIR transmission spectra of the cold mirror, hot mirror and hot extended mirror.

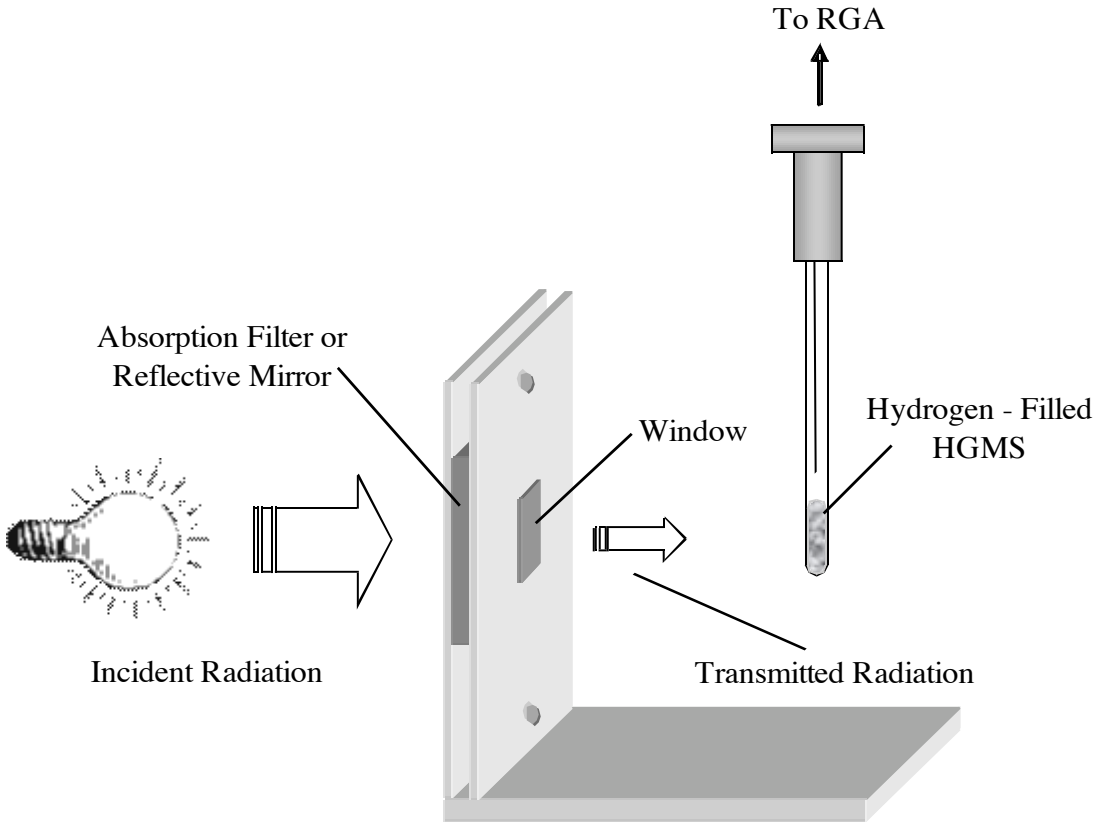


Figure 20. Schematic of the sample holder used for photo-outgassing experiments of controlled wavelength.

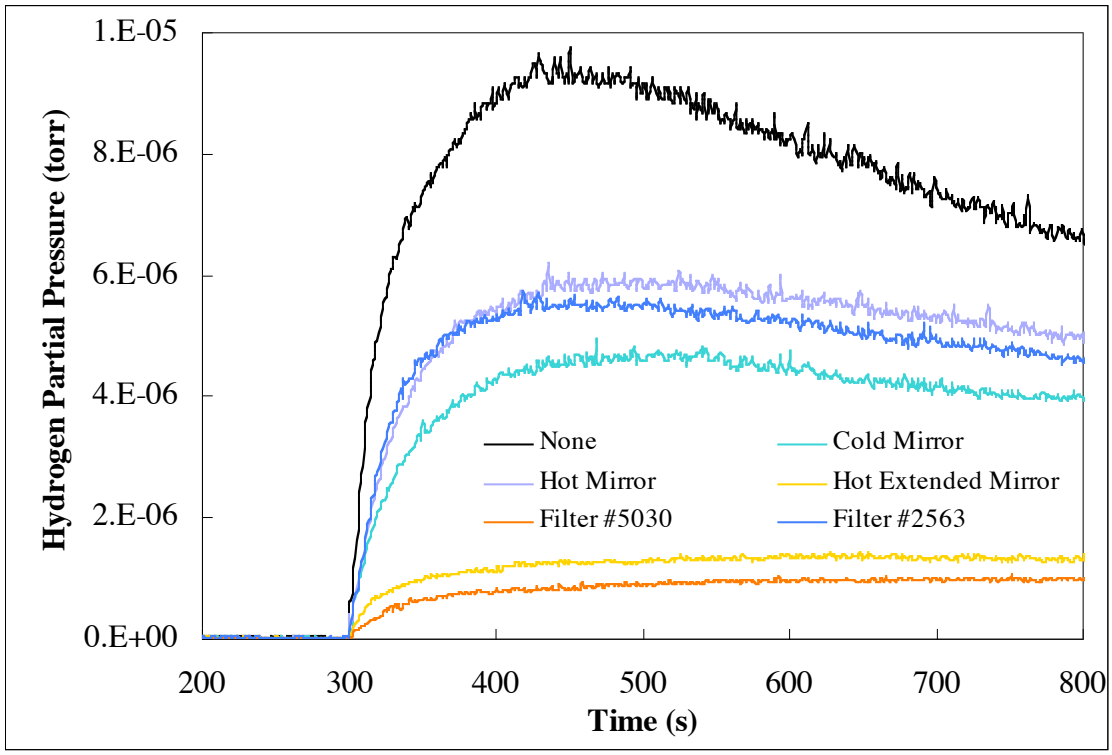


Figure 21. Photo-outgassings using specific wavelengths of light from the 5 wt% nickel oxide-doped HGMS filled with 700 Torr of hydrogen at 400°C.

A hydrogen retention study was conducted in which all compositions were equilibrated with hydrogen under identical conditions and held at either room temperature or 50°C for 5 weeks. A comparison of the hydrogen released from fully saturated HGMS to those after 5 weeks is shown in Figures 22 and 23. Very little hydrogen is released from samples stored at room temperature. As much as 65 – 95% remains in the HGMS after 5 weeks for samples stored at 50°C.

A number of samples of the amber and 5 wt% iron, nickel and cobalt oxide-doped HGMS were shipped to Savannah River National Laboratory, where they were filled to 1,500 psi at 400°C. Samples filled to 1,500 psi exhibit a small amount of breakage, but no more than those samples as-received directly from MoSci (Figure 24). Hydrogen is release is immediate with the onset of lamp exposure as shown in Figure 25 for 5 wt% CoO- doped HGMS. Similar behavior is also exhibited by iron and nickel oxide-doped HGMS. The relative amounts of hydrogen released during thermal and photo- outgassing are comparable (Figure 26), except for the undoped HGMS, which is to be expected.

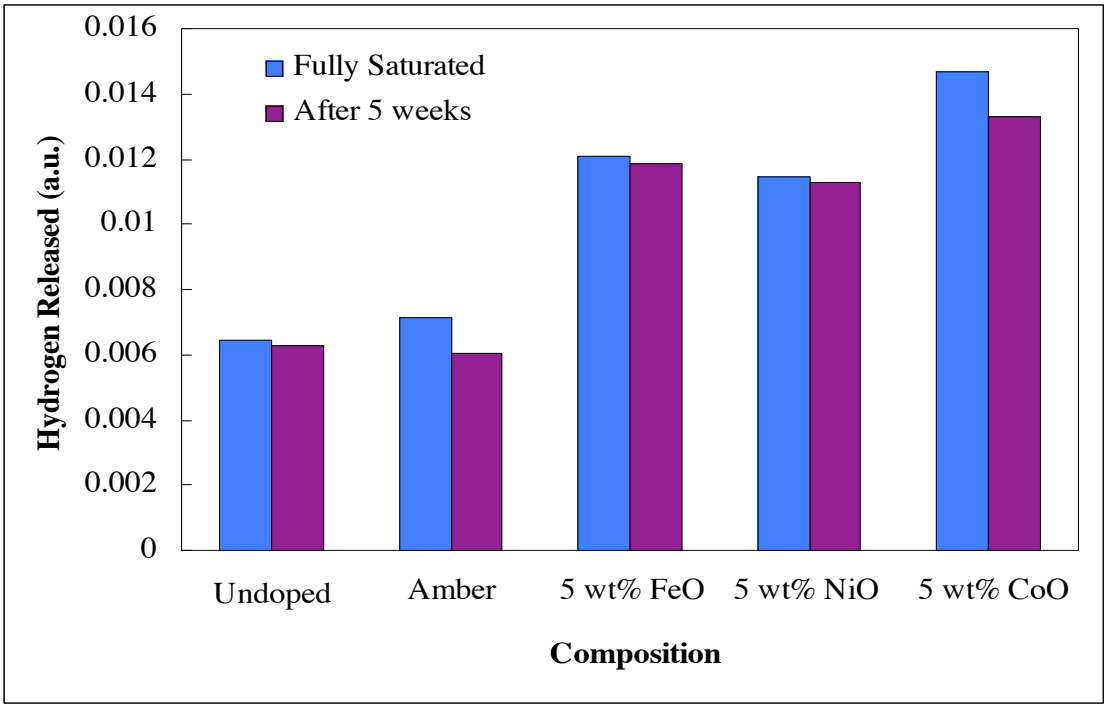


Figure 22. Comparison of hydrogen released from filled HGMS and those after 5 weeks held at room temperature.

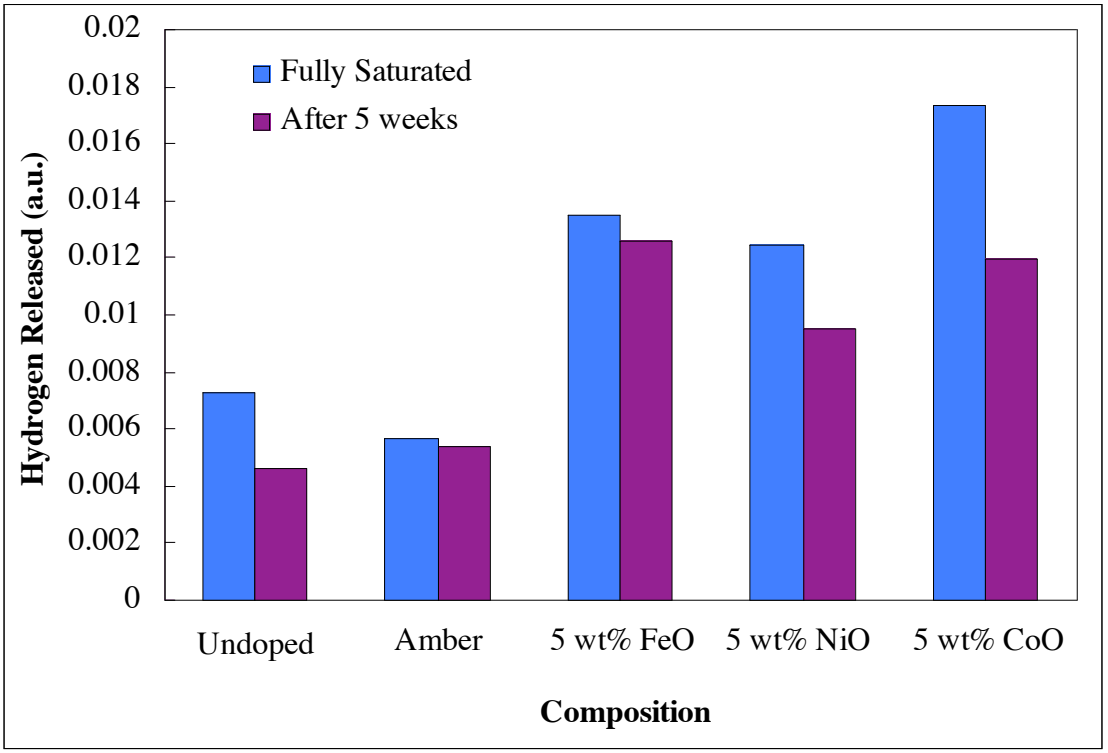
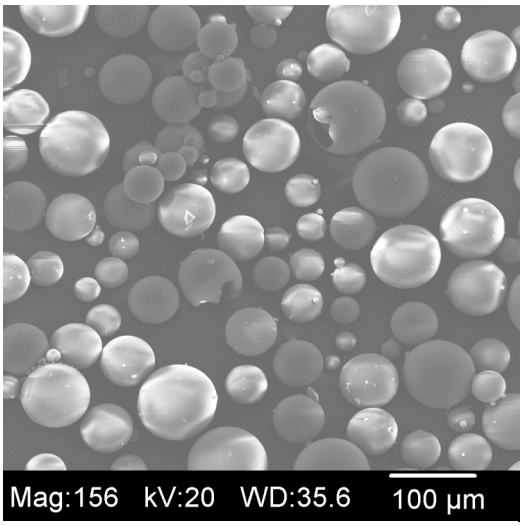
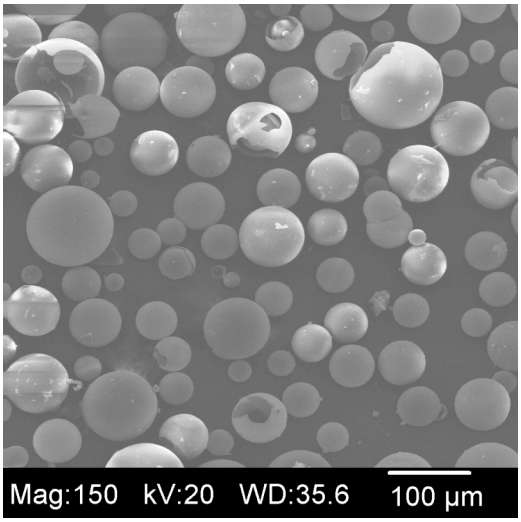


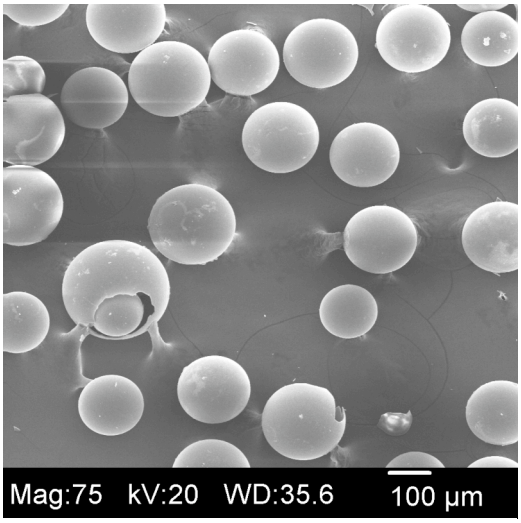
Figure 23. Comparison of hydrogen released from filled HGMS and those after 5 weeks held at 50°C.



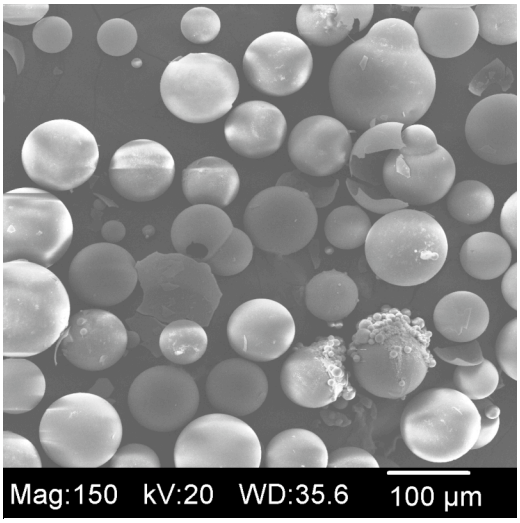
Amber HGMS



5 wt% iron oxide-doped HGMS



5 wt% nickel oxide-doped HGMS



5 wt% cobalt oxide-doped HGMS

Figure 24. SEM micrograph of as-received amber and 5 wt% doped HGMS filled to 1,500 psi.

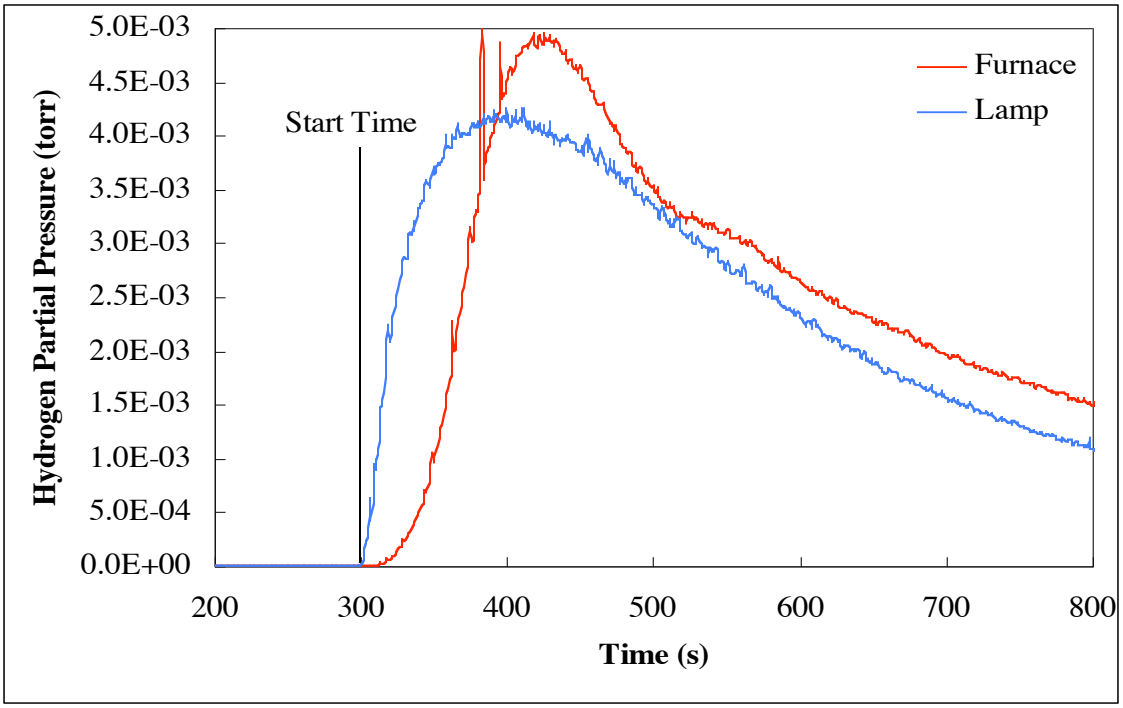


Figure 25. Comparison of hydrogen thermal (400°C) and photo-outgassing of 5 wt% CoO- doped HGMS filled to 1,500 psi at SRNL.

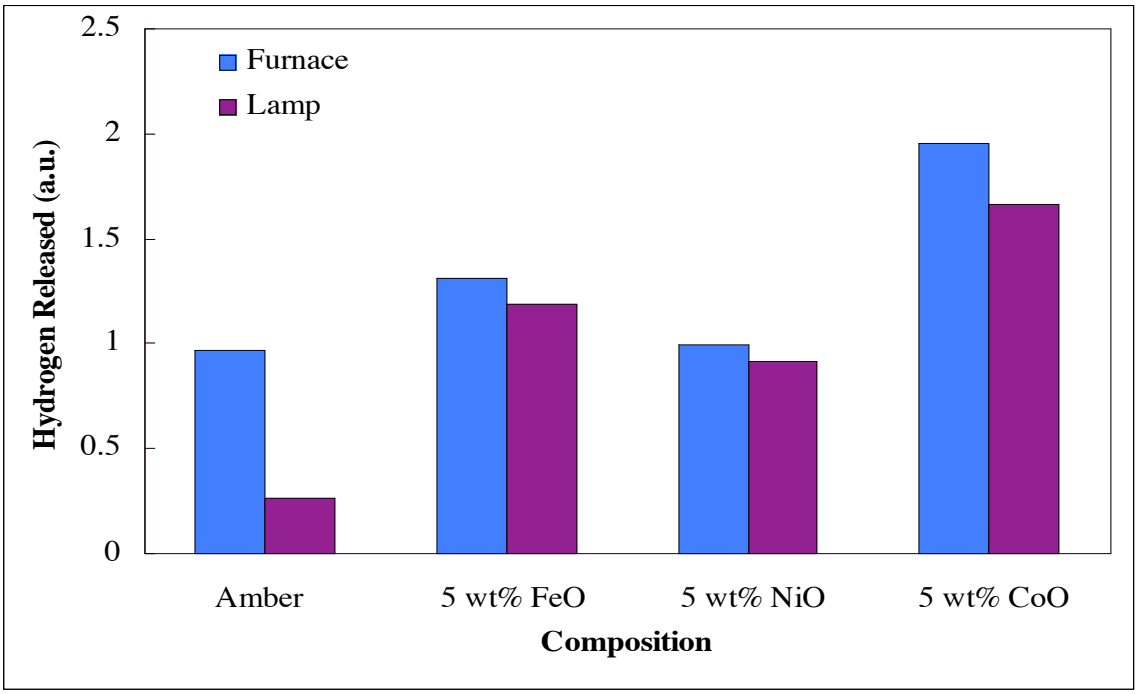
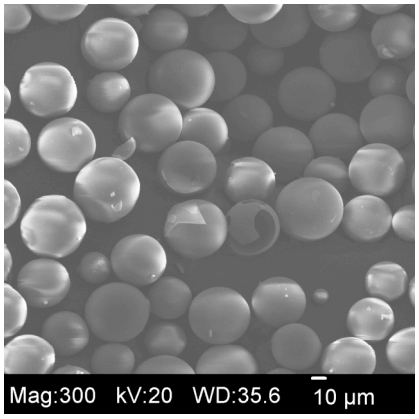
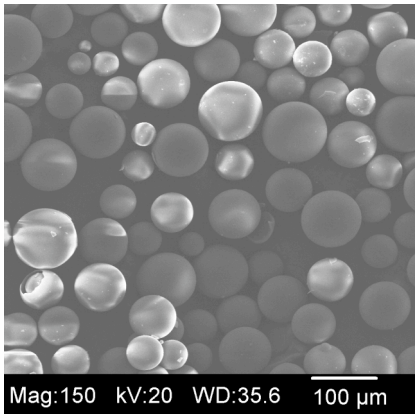


Figure 26. Comparison of the amount of hydrogen released from HGMS filled to 1,500 psi via thermal and photo-outgassing.

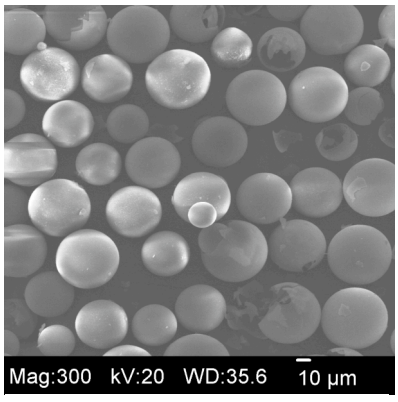
Savannah River National Laboratory also successfully filled amber and 5 wt% cobalt oxide-doped HGMS with hydrogen at 5,000 psi and 400°C. Samples of the amber and 5 wt% cobalt oxide-doped HGMS were separated into size fractions of less than 50 μm, 50-100 μm and greater than 100 μm prior to shipping to SRNL. It should be noted that the amber sample did not contain enough HGMS greater than 100 μm to send to SRNL. The amber samples filled to 5,000 psi show very little signs of breakage, which differs from the results found for the 5 wt% cobalt oxide-doped samples in which failure occurs for all size fractions as shown in Figure 27. More than half of the cobalt HGMS greater than 100 μm in diameter did not survive the 5,000 psi pressurization. The survival rate does increase with decreasing sphere diameter.



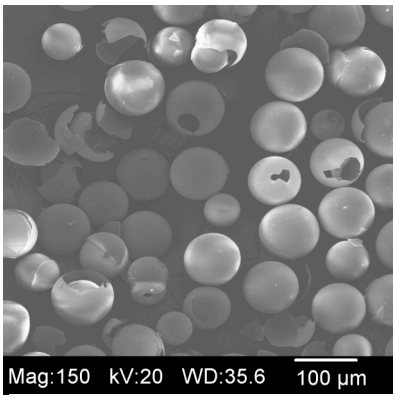
Amber HGMS (<50 µm)



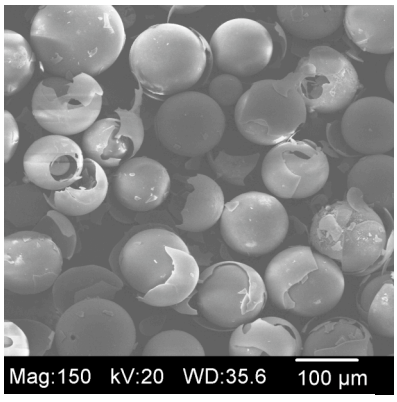
Amber HGMS (50-100 µm)



5 wt% cobalt oxide-doped HGMS (<50 µm)



5 wt% cobalt oxide-doped HGMS (50-100 µm)



5 wt% cobalt oxide-doped HGMS (>100 µm)

Figure 27. SEM micrograph of as-received amber and 5 wt% cobalt oxide-doped HGMS filled to 5,000 psi.

As was found for the 5 wt% cobalt oxide-doped HGMS filled to 1,500 psi, the hydrogen release of the HGMS filled to 5,000 psi is immediate upon lamp exposure (Figure 28). There is a considerable increase in the initial rate of photo-outgassing with increasing fill pressure as shown in Figure 29. The initial outgassing response for the samples containing higher pressures of hydrogen is much more rapid than for samples containing only 700 torr of hydrogen.

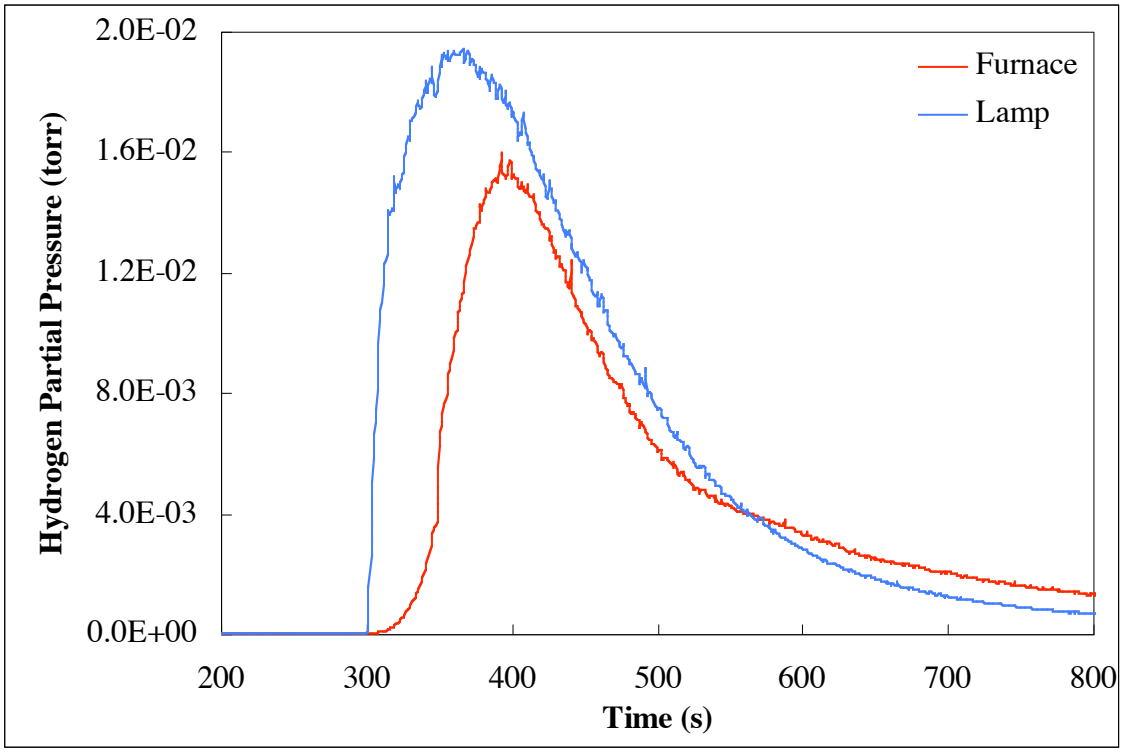


Figure 28. Comparison of hydrogen thermal (400°C) and photo-outgassing of 5 wt% CoO- doped HGMS filled to 5,000 psi at Savannah River National Laboratory.

A limited study was conducted to determine the potential for use of light to fill empty HGMS (photo-induced ingassing). The amount of hydrogen released from 5 wt% cobalt oxide-doped HGMS filled under photo conditions is less than that of those treated thermally at 400°C for 30 minutes (Figure 30) but is greater than that if the filling temperature is reduced to 250°C. The trends in the 5 wt% iron and nickel oxide-doped HGMS are not as conclusive, however, but it is clear that photo-induced ingassing of undoped HGMS does not result in an appreciable subsequent hydrogen release, i.e. at best very little hydrogen enters the HGMS under those conditions.

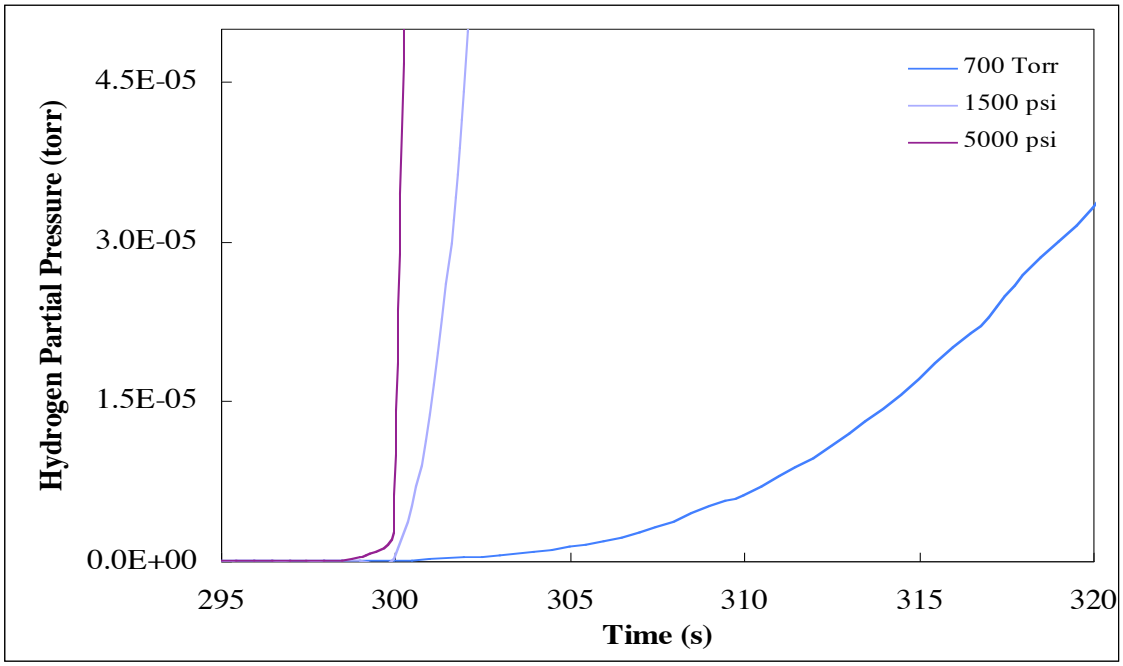


Figure 29. Influence of the fill pressure on the initial rate of photo-outgassing of the 5 wt% cobalt oxide-doped HGMS.

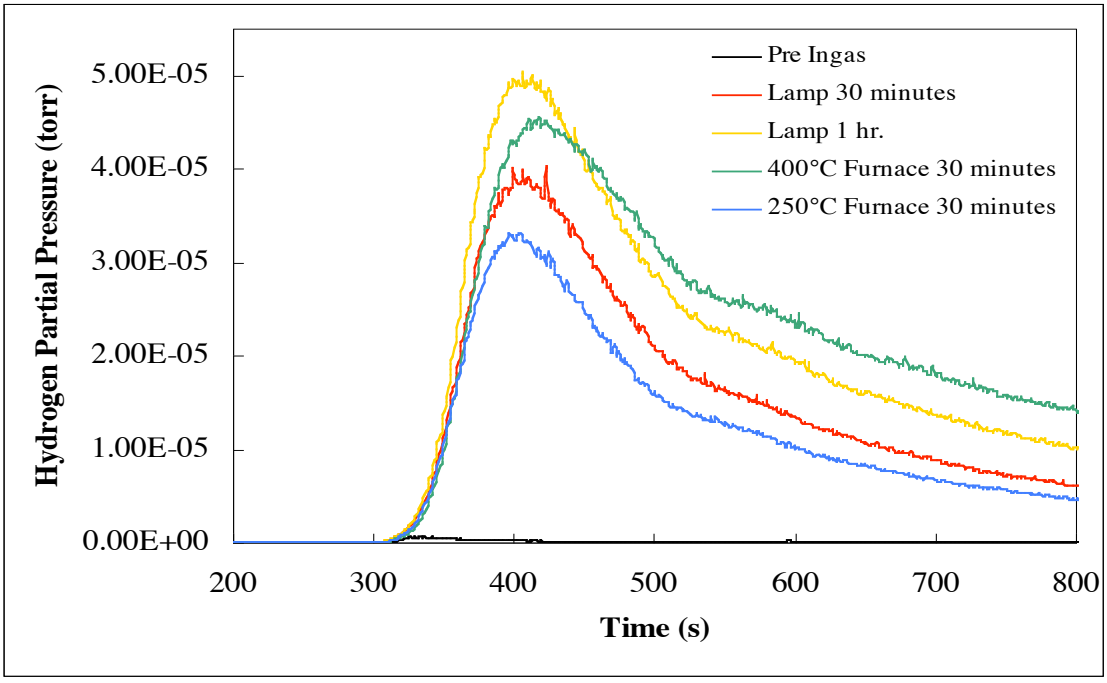


Figure 30. The outgassing behavior of 5 wt% cobalt oxide-doped HGMS filled under the photo and thermal conditions noted.

Color changes were noted in samples of the nickel doped spheres following a number of filling/outgassing cycles. Samples of the 5 wt% doped HGMS were thus treated for a total of 335 hours at 500°C. The 5 wt% nickel oxide-doped HGMS turned black, with a somewhat metallic appearance, while the 5 wt% cobalt and iron oxide-doped microspheres turned dark blue/gray and green/gray in color, respectively. The treated 5 wt% nickel and cobalt oxide-doped HGMS exhibit a small increase in the amount of hydrogen released during photo-outgassing as shown in Figure 31 for the nickel doped spheres. There is no change in the amount of hydrogen released from the 5 wt% iron oxide-doped HGMS. Other measurements indicate that the 5 wt% nickel and cobalt oxide-doped HGMS become magnetic after successive hydrogen treatments.

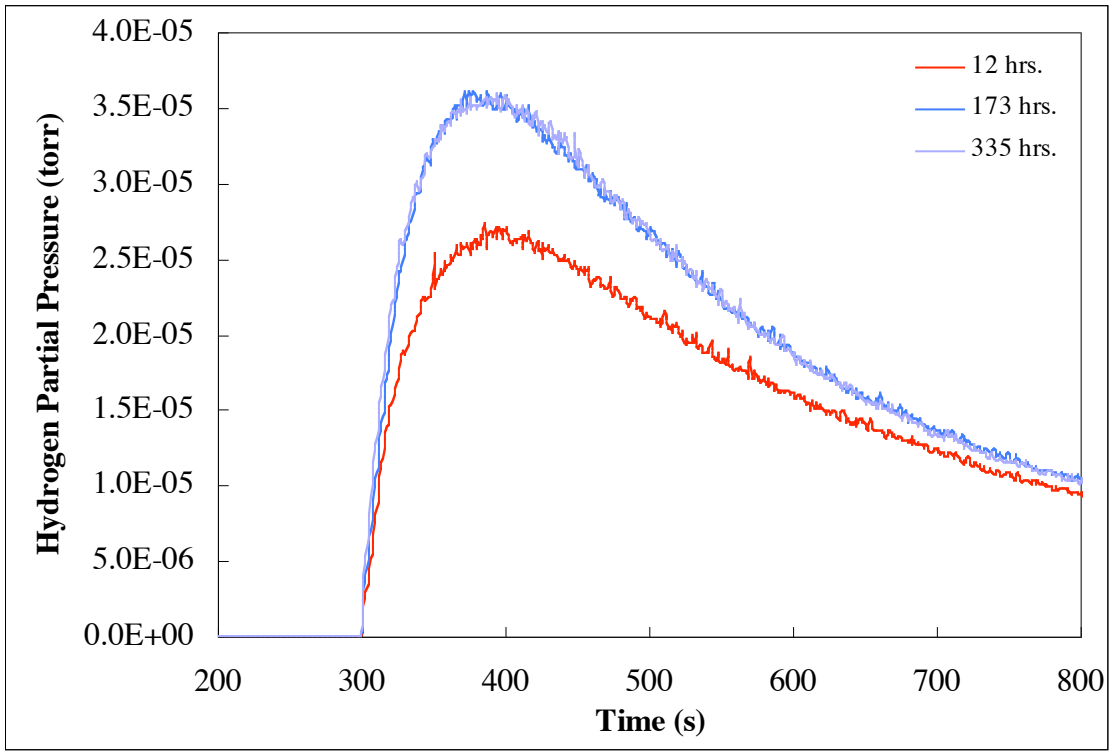


Figure 31. Photo-outgassing from 5 wt% nickel-oxide doped HGMS as a function of hydrogen treatment time.

A PhD thesis reporting the results of this work has been completed and defended. Dr. Raszewski has received her degree and accepted a position at SRNL.

Conclusions:

Significant data regarding photo-induced hydrogen diffusion in HGMS have been obtained, validating the concept underlying this project. Photo-induced hydrogen outgassing behavior occurs in all HGMS doped with 1 and 5 wt% iron, nickel, or cobalt oxide, with CoO yielding the most impressive results. The improvement in outgassing behavior obtained by use of CoO may or may not be offset by the cheaper cost of iron oxide. The spectrum and source of the IR lamp has been found to be extremely important, with supposedly similar lamps from different manufacturers producing very different results. Development of this process to a commercial level will require additional knowledge of lamp effects in order to select the most efficient lamp for this application. Wavelengths in the range 1500-2200 nm are thought to be most responsible for the photo-induced response. The amount of hydrogen released increases exponentially with voltage supplied to the IR source, i.e. with lamp intensity and shifts in the light spectrum, allowing tight control over the rate of hydrogen supply by a simple rheostat. Hydrogen losses are minimal over time at both room temperature and 50°C. HGMS have been successfully filled to 1,500 psi and 5,000 psi at Savannah River National Laboratory. Limited results suggest that photo-induced ingassing may be an efficient method for filling HGMS. Extended hydrogen treatments at 500°C result in color changes of the 5 wt% doped HGMS and slightly enhanced photo-outgassing in the 5 wt% nickel and cobalt oxide-doped HGMS. The 5 wt% nickel and cobalt oxide-doped HGMS also become magnetic, suggesting that metal nanoparticles are formed by reduction by the hydrogen gas entering the glass. Success of this project will allow development of HGMS for large scale storage of hydrogen to serve as a source of fuel for fuel cells and other methods of utilizing hydrogen as a fuel.

Results of this study establish the potential for commercial development of doped hollow glass microspheres coupled with photo-induced diffusion as a method for storing, transporting, and delivering hydrogen on demand. The inherent safety of the concept due to the distributed nature of the hydrogen combined with the inexpensive, non-toxic, and recyclable nature of the materials all indicate that this method can produce a superior product/process for a number of applications in the hydrogen economy.

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4. F.C. Raszewski, M.M. Hall and J.E. Shelby, “Thermal and Photo – Induced Outgassing of Hollow Glass Microspheres.” Glass and Optical Materials Meeting 2006, Greenville, May 16 – 19, 2006.

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7. F. C. Raszewski, “Hydrogen Storage in Hollow Glass Microspheres” PhD Thesis, Alfred University, April, 2007.

List of Acronyms:

HGMS – hollow glass microspheres
RGA – residual gas analyzer
SRNL – Savannah River National Laboratory